Journal of Hazardous Materials 328 (2017) 70–79

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Effects of superabsorbent polymers on the fate of fungicidal carbendazim in soils

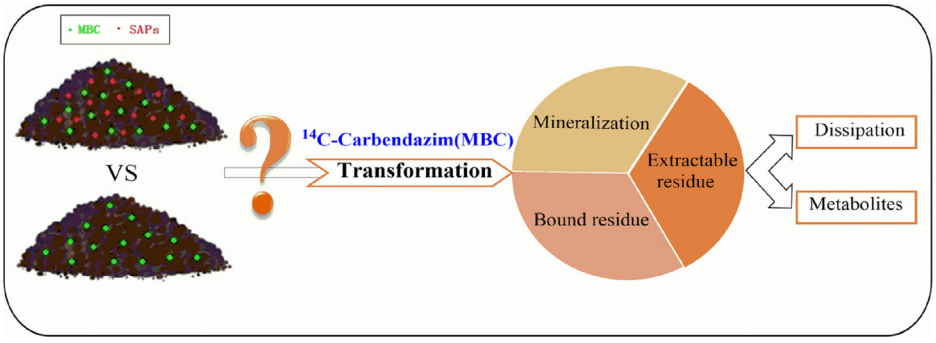
Yatian Yang, Haiyan Wang*, Lei Huang, Sufen Zhang, Yupeng He, Qi Gao, Qingfu Ye*

Institute of Nuclear Agricultural Sciences, Key Laboratory of Nuclear Agricultural Sciences of Ministry of Agriculture and Zhejiang Province, Zhejiang University, Hangzhou 310029, China

HIGHLIGHTS

- SAPs affected the transformation of MBC in oxic soils.
- MBC mineralization was obviously inhibited in loamy and saline soils with SAPs.
- SAPs enhanced the dissipation of MBC in acidic clayey soil.
- SAPs increased the bound residue of MBC in soils.
- Soil microbial state was changed after treated with MBC and SAPs during incubation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 September 2016
Received in revised form
27 December 2016
Accepted 28 December 2016

Keywords:
Superabsorbent polymers (SAPs)
Carbendazim
Transformation
Metabolites

ABSTRACT

Superabsorbent polymers (SAPs) have been extensively used as soil amendments to retain water, and they often coexist with pesticides in agricultural fields. However, effects of SAPs on the fate of pesticides in soil remain poorly understood. In this study, a laboratory experiment was conducted to evaluate the effects of SAPs on the transformation of ^{14}C-carbendazim in soils. The results showed that compared to the SAPs-free control, 11.4% relative reduction of ^{14}C-carbendazim extractable residue was observed in red clayey soil with SAPs amendment after 100 days of incubation ($p < 0.05$). Carbendazim dissipation was enhanced by 34.7%, while no obvious difference was found in loamy soil and saline soil ($p > 0.05$). SAPs changed the profiles of major metabolites (2-aminobenzimidazole and 2-hydroxybenzimidazole) to some extent. After 100 days of SAPs treatment, the mineralization of ^{14}C-carbendazim was significantly reduced by 37.6% and 41.2% in loamy soil and saline soil, respectively, relative to the SAPs-free treatment ($p < 0.05$). SAPs increased the bound residue of carbendazim by 11.1–19.1% in comparison with SAPs-free controls. These findings suggest SAPs amendments significantly affected the fate of carbendazim and attention should be given to the assessment of environmental and ecological safety of pesticides in SAPs-amended soils.

1. Introduction

Superabsorbent polymers (SAPs) can absorb and retain up to several hundred times their weight of water [1]. Due to their excellent water retention abilities, SAPs have been widely utilized in many areas such as medicine, horticulture, sanitary products, and agriculture [2–5]. In particular, SAPs are usually applied as soil con-

Abbreviations: SAPs, superabsorbent polymers; MBC, carbendazim; POPOP, 1, 4-bis (5-phenyloxazoly-2-yl)-benzene; PPO, 2, 5-diphenyloxazole; ER, extractable residue; BR, bound residue; St-g-PAM, starch-g-polyacrylamide; MBA, *N*, *N*'-methyl bis-acrylamide; 2-AB, 2-aminobenzimidazole; H-AB, 2-hydroxybenzimidazole.

* Corresponding authors.
E-mail addresses: qfye@zju.edu.cn (Q. Ye), wanghaiyan@zju.edu.cn (H. Wang).

http://dx.doi.org/10.1016/j.jhazmat.2016.12.057
0304-3894/

ditioner in agriculture to hold soil moisture, improve soil stability or aeration, and prevent soil erosion [6]. Moreover, SAPs have been employed in combination with pesticides to control their release rates in order to promote the efficiency use of both pesticides and water [7,8]. Therefore, it is common for pesticides and SAPs to coexist in agricultural fields.

SAPs are macromolecule polymers, capable of serving as an organic carbon source for soil microorganisms [8]. The presence of SAPs and other organic amendments could alter soil microbial communities, and hence influence the environmental behaviors of pesticides in soils. Marin-Benito et al. [9] demonstrated that amendment with mushroom substrates enhanced microbial activity and promoted the dissipation of fungicides in the vineyard. Achtenhagen et al. [10] found that SAPs amendments could significantly increase the sorption of ^{14}C-imazalil in soils and stimulate microbial activity. Additionally, SAPs contain certain functional groups, such as carboxylic acid, carboxamide, hydroxyl, amine, and imide groups, which could interact with pesticides or the soil matrix via catalysis with soil enzymes and microorganisms [11]. Thus, SAPs might influence the biological/abiotic degradation behavior of pesticides in soils. The addition of SAPs would generate unpredictable impacts on the fate and ecological effect of pesticides. Thus, the environmental fate, biological effects, and toxicity of commercially available pesticides in SAPs-amended soil must be clarified.

Carbendazim, a broad-spectrum benzimidazole fungicide, is widely used to control fungal diseases in crops and vegetables [12]. Carbendazim could adsorb strongly to soils, and is moderately persistent in crops and soils, posing risks to agroecosystem and human health [13]. However, little is known of the effects of the co-existence of SAPs and carbendazim on the environmental fate of carbendazim in soils. Therefore, we used self-synthesized SAPs combined with ^{14}C-labelled carbendazim to evaluate the transformation of carbendazim, including characterization of dissipation of the parent compound, the kinetic changes of metabolic products and extractable residue (ER), non-extractable/bound residue (BR) and mineralized ^{14}C-CO_2 in soils amended with SAPs during the incubation.

2. Material and methods

2.1. Chemicals

^{14}C-Carbendazim (methyl (1H-benzo[d]imidazol-2-yl-2-^{14}C) carbamate; radio-chemical and chemical purity >97%; 51 mCi/mmol specific radioactivity) was purchased from ChemDepo Incorp. (Camarillo, CA). The ^{14}C-labeling position of carbendazim was 2-[^{14}C]-benzimidazole nuclei. Non-labelled carbendazim (chemical purity > 96%) was obtained from Sigma-Aldrich (Munich, Germany). Glycol ether, ethanolamine, methanol, hydrochloric acid, and sodium hydroxide were all analytical grade reagents. Scintillation grade reagents of 1,4-bis (5-phenyloxazoly-2-yl)-benzene (POPOP) and 2, 5-diphenyloxazole (PPO) were obtained from Arcos Organics (Geel, Belgium). Scintillation cocktail I consisted of 0.5 g POPOP, 7.0 g PPO, 650 mL dimethyl benzene and 350 mL glycol ether. Scintillation cocktail II consisted of 0.5 g POPOP, 7.0 g PPO, 550 mL dimethyl benzene, 275 mL glycol ether, and 175 mL ethanolamine. Acetonitrile, water and glacial acetic acid were chromatography grade. The stock solution of ^{14}C-carbendazim was prepared by mixing non-labelled carbendazim and the labelled in methanol with a final specific activity of 4.625×10^4 Bq mg^{-1}.

2.2. Soil and SAPs

Three samples of natural soils were collected from the first 0–15 cm-layer of soil from agricultural fields in Hangzhou (fluvio-marine yellow loamy soil), Cixi (coastal saline soil), and Longyou (red clay soil), Zhejiang Province, China. These soils are abbreviated herein as S_1, S_2, and S_3. Some selected physico-chemical properties of soils were determined using standard methods [14,15] and summarized in Table 1. All soils were air-dried, passed through a 2-mm sieve and stored at room temperature before use.

SAPs, starch-graft-polyacrylamide (St-g-PAM) superabsorbent crosslinked by *N*,*N*-methyl bisacrylamide were prepared using 10 MeV simultaneous electron beam irradiation at room temperature and subsequent alkaline hydrolysis [16]. The swelling ratio of SAPs (deionized water) was approximately 1000 g g^{-1}. SAPs were dried at room temperature in a vacuum drying apparatus.

2.3. Soil treatment and incubation experiment

The incubation experiment was carried out under aerobic conditions as per the OECD guideline 307 [17]. Pre-incubation was conducted at 25 ± 1 °C for 10 days and all soil water content was separately adjusted to 40% of the water-holding capacity. SAPs were then amended to 0.5‰ (w/w) in soils. Carbendazim was applied to the soils by dissolving in methanol and fully mixing with soil samples at 4 mg kg^{-1} (approximately 300 g soil, dry weight equivalent). Subsequently, soil moisture content was regulated to 60% of the water-holding capacity. Similarly, the SAPs-free treatment with carbendazim underwent the above procedures. The uniformity of ^{14}C-distribution was confirmed by the combustion of 1.0 g of the soil subsample (three replicates) in a biological oxidizer (RJ Harvey Instruments, Hillsdale, NJ). Blank controls without carbendazim and SAPs were used for microbial analysis and subjected to the same process. The evenly mixed soils were transferred to 500 mL brown jars fitted with a flow-through apparatus for trapping solutions, as described by Fu et al. [18]. The experimental settings were placed in an incubator at 25 ± 1 °C and ventilated periodically. Soil subsamples (10 g, dry weight equivalent) were collected from each soil container at intervals of 0, 3, 6, 13, 20, 30, 45, 60, 80, and 100 days after treatment (DAT) and the experiments were conducted in triplicate for each treatment. An equivalent quantity of distilled water was added to maintain soil moisture at 60%, and all the trapping solutions were replaced regularly with fresh solutions at each sampling time. The trapping solutions were preserved to measure the radioactivity on a liquid scintillation counter (LSC, Quatalus-1220, Perkin-Elmer, Turku, Finland). An aliquot of 1-mL for each trap was obtained and added to 15 mL of cocktail I, then stored in the dark for 24 h before counting to avoid chemiluminescence. Only the ^{14}C-CO_2 solution was detected the radioactivity in all the traps. Soil subsamples were removed to determine the radioactivity of extractable, and non-extractable residue. The amount of ^{14}C-carbendazim present in the form of parent and/or intermediates during sampling.

2.4. Soil extraction and combustion analysis

Soil samples (10.0 g, dry weight) per treatment were processed in a polypropylene centrifuge and sequentially extracted following a modified procedure derived from Helweg [19] and Wang et al. [20]. Briefly, soil samples were extracted three times with 30 mL of methanol/0.1 M hydrochloric acid solution (4:1, v/v), blended thoroughly, and shaken for 2 h at 120 rpm on a rotary shaker, centrifuged at 6000*g* for 5 min. The deposits were then similarly re-extracted by shaking with methanol, and ethyl acetate, consecutively, until no more ^{14}C-radioactivity was detected in the extracts. The recovery extraction of ^{14}C activity was approximately